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FISCHER-TROPSCH SYNTHESIS ON RU/NAY CATALYSTS: EFFECT OF THE ACIDITY OF THE ZEOLITE

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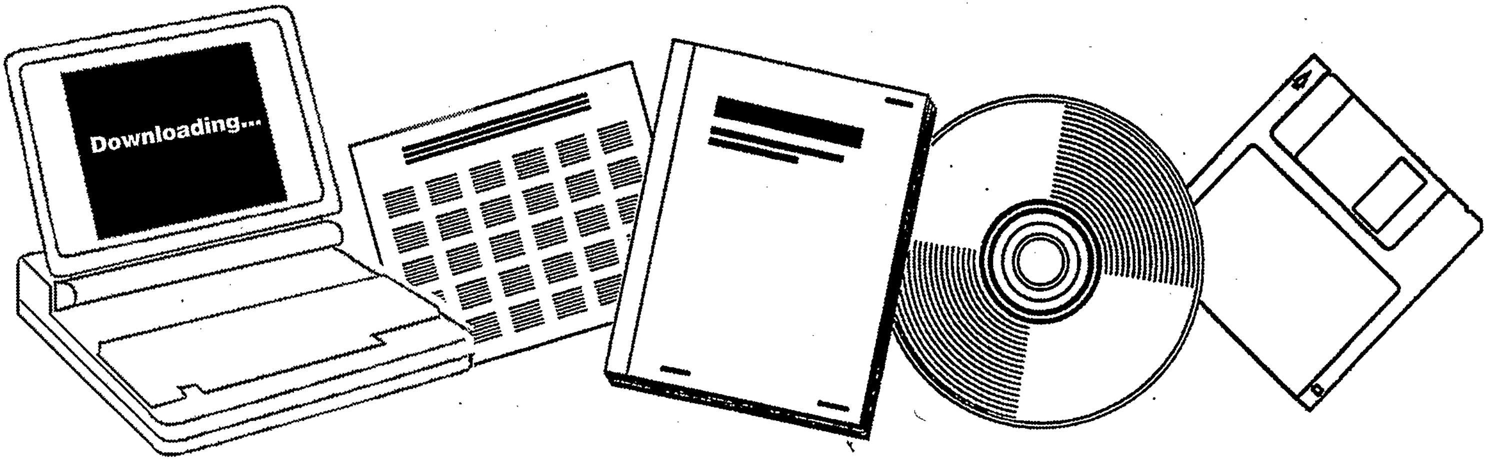

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ABSTRACT

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Key words: Zeolite, Catalysis, Ruthenium

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FISCHER-TROPSCH SYNTHESIS ON Ru/NaY CATALYSTS: EFFECT OF THE ACIDITY OF THE ZEOLITE

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A series NaY zeolites with different Si/Al ratio were used to support the Ru catalysts. Both the activity/selectivity of Ru in F-T Synthesis and the suppression of hydrogen may be related to the acid strength of the OH group present, which is a function of the Si/Al ratio of the zeolite.

1. INTRODUCTION

Ruthenium is well known to be one of the most active catalysts for the F-T synthesis. While silica, alumina, and other metal oxides have been widely used as supports for transition metals, the use of zeolite supports has been fairly limited. Due to their high surface areas, high metal dispersion can be easily maintained on such supports.(1-4) In addition, owing to the incorporation of the metal particles in a geometrically-restricted environment, zeolite-supported catalysts can exhibit shape selectivity.(6,11) Also, owing their acidic nature, secondary reactions such as isomerization can influence the product distribution.(2-3,9-10) The behavior of transition metals in zeolite is complex and not fully understood at this time. Although the previous studies suggested ways in which the zeolite support may affect adsorption and catalytic properties of Ru catalysts, the trends for these support effects remain still inconsistant and ambiguous. The present study was undertaken to investigate systematically the influence of Si/Al ratios on F-T synthesis over zeolite-supported Ru catalysts.

2. EXPERIMENTAL

The NaY zeolite was obtained from Strem Chemicals. Dealuminated NaY samples were prepared in an aqueous solution of H_4EDTA refluxed at 363K for 24 hours with continuous stirring. Following dealumination samples were washed with hot water to wash out soluble products and then dried at 333 K overnight.(7)

A conventional ion exchange method was used to load Ru into zeolites. $Ru(NH_3)_6Cl_3 1.5H_2O$ was dissolved in a weakly acidic HCl aqueous solution (pH=4.5). This solution was then mixed with the zeolite and stirred continuously for 50 hr at room temperature. The solid was then filtered, thoroughly washed with deionized water in order to free it of Cl ions, and dried in air overnight at 313K. The catalysts were decomposed under vacuum ($1x10^{-6}$ Torr) by heating to 673 K (0.5 K/min) and holding at that temperature for 2 hours. The samples were then reduced in hydrogen for one hour at that maximum temperature.

The Ru metal loadings of the catalysts were determined by

AA.(5) Chemisorption of H and CO were conducted at ambient temperature in a glass adsorption system capable of achieving a vacuum of ca. 1×10^{-6} torr.(2)

Fischer-Tropsch Synthesis was carried out in a turbular microreactor made from a stainless steel tube of 3/8 in. diameter. Reaction was carried out at atmospheric pressure and 493-573 K using a 1:1 mixture of H_2/CO following at GHSV=1800-2400. Under these conditions, CO conversion was found to be lower than 10%.

3. RESULTS AND DISCUSSION

3.1 Gas Chemisorption

The result of hydrogen and carbon monoxide chemisorption for the various Ru catalysts are given in Table 1. It has been

Table 1. Catalysts Characteristics Based on Gas Chemisorption.

No.	Metal loading (wt%)	Si/Al Ratio	H/Ru	CO/Ru
1	3.1	2.4	0.62	2.34
2	2.8	3.0	0.47	2.18
3	2.9	3.5	0.31	1.96
4	3.2	4.2	0.29	2.43
5	2.9	4.5	0.17	3.21
6	3.1	5.3	0.13	2.78

reported previously(12) that suppresion of hydrogen chemisorption could be significant for most-zeolite-supported catalysts. The strength of acidic hydroxyl protons (correlated with ths Si/Al ratio) are suggested to be the reason for hydrogen chemisorption suppresion. Our results are in agreement with this conclusion. In addition, CO/H ratios have been found to be a function a particle size.(13) Thus a comparison of the CO/H ratios in Table 1 suggests that the dispersion of the Ru in the various Y zeolites are high and similar.

3.2 Catalytic Activity

Because of the possible suppression of hydrogen chemisorption on Ru/NaY zeolites, the specific activities were used for comparison. As shown in Table 2, both the specific activities and activation energies are slightly decreased with

Table 2. Effect of the Si/Al Ratio on F-T Synthesis.

No.	Si/Al Ratio	$-r_{CO}$ (μmol/s·gcat.)	$E_{act.}$(KJ/mol)
1	2.4	1.87	94
2	3.0	1.64	76
3	3.5	1.42	50
4	4.2	1.21	52
5	4.5	1.18	48
6	5.3	0.94	50

reaction condition: 1atm, 523 K, $H_2/CO=1$.

increasing Si/Al ratio. Jacobs et al.(6) reported that for Ru/zeolite catalysts the activity for methanation decreased with increasing Si/Al ratio of the zeolite support, provided the temperature of reduction was only 573 K. They attributed their results to an electronic metal-zeolite interaction which can influence the electron-deficient character of the metal crystals. The electron-deficient character of the metal causes a suppresion of hydrogen chemisorption and results in a decrease of secondary hydrogenation of the primary formed olefins.

3.3 Catalyst selectivity

The C3 fraction was selected for comparing the olefinic fractions yielded by the Ru catalysts, because, as expected, the C2 fraction was mainly paraffinic and the olefin fractions of hydrocarbons having more than three carbon atoms were

Table 3. Product Selectivity of Ru/NaY in CO Hydrogenation.(a)

No.	Si/Al ratio	$C_{3=}/C_3$	i-C_4(%)(b)
1	2.4	2.5	28
2	3.0	4.5	34
3	3.5	4.6	44
4	4.2	5.6	47
5	4.5	5.4	47
6	5.3	6.8	57

(a) reaction condition: 1 atm, 523 K, H_2/CO=1.

(b) in C_4 fraction.

complicated by possible secondary isomerization reactions.

The Si/Al ratios of Y zeolite were found to have a strong influence on the olefin-to-paraffin ratio. The amount of isobutene in the C4 fraction shown in Table 3 is also related to the Si/Al ratios of zeolites. Since the acid strength of the hydroxyl groups increases with an increase in the Si/Al ratio, it is suggested that the strength of OH groups in zeolites can influence the formation of isobutene. It has also suggested that it is the cause of chemisorption suppresion. These results suggest that primary hydrocarbon products are olefins which can undergo either direct secondary hydrogenation or skeletel isomerization and hydrogenation.

Leith(9-10) has also reported that the olefin selectivity of zeolite-supported ruthenium in the carbon monoxide hydrogenation reaction is enhanced when potassium and cessium are exchanged into Y zeloites. He interpreted his results in terms of a lowering of the hydrogenation activity of the metal as a result of a decrease in the eletron deficient character of the metal particle brought about by the introduction of alkali cations into the zeolite. Dealumination of Y zeolite is known to enhance its acidic and electron acceptor character.(7) Hence small metal particles exchanged in these zeolites should become metal particle electron transfer between the Ru metal and electron-acceptor sites (OH group) or due to a perturbation of the electronic structure of the metal by the high electronic fields.

4. CONCLUSIONS

The results of this study show that Si/Al ratio of zeolite support has pronounced effects on the activity and selectivity of Ru for CO hydrogenation. The specific activity appears to be decreased with increasing Si/Al ratio of zeolite. At the same time the hydrocarbon product selectivity shifts to the unsaturated hydrocarbons. These results toward isobutane as the acidity of the zeolite increased is to be expected from the well-known isomerization activity of acidic zeolites. Both the formation of isobutane and the suppression of hydrogen chemisorption may be related to the acid strength of the OH groups present, which is a function of the Si/Al ratio of the zeolite.

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